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(54) Catalyst systems for the polymerization and copolymerization of alpha-olefins

Katalysatorsysteme für die (Co)Polymerisation von Alpha-Olefinen

Systèmes catalytiques pour la (co)polymérisation d'alpha-oléfines

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- **STEVENS J. C.: "Insite Catalysts Structure/Activity relationships for Olefin Polymerization" STUDIES IN SURFACE SCIENCE CATALYSIS., vol. 89 (CATALYST DESIGN FOR TAILOR MADE POLYOLEFINS), - 1994 pages 277-284, XP002054520**
- **DIAS H V R ET AL: "Preparation of Group 4 metal complexes of a bulky amido-fluorenyl ligand" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 508, no. 1, 8 February 1996, page 91-99 XP004036211**

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[0001] The present invention relates to organometallic catalysts, to the process for preparation thereof and their use for the polymerization and copolymerization of ethylene and alpha-olefins in industrial production plants.

[0002] There is a great variety of processes and catalysts useful for the homo- and copolymerization of olefins. Catalytic systems such as Ziegler-Natta are typically able to produce polyolefins with high molecular weight and broad distribution of molecular weight. However, for many industrial applications it is of the greatest importance to obtain polyolefins characterized by a high molecular weight, and narrow molecular weight distribution. Besides, with these Ziegler-Natta type of catalysts, to obtain copolymers with fit comonomer contents it is necessary to use high comonomer/monomer molar ratios in the feed and as a consequence the industrial process becomes enormously more expensive.

[0003] In the last years there has been the development of organometallic catalytic metallocene systems, that, combined with non-coordinative anions, alkylaluminoxanes or boron perfluorinated compounds (US 4542199 and EP 426637) allow to obtain polyolefins with narrow distributions of molecular weight and high molar comonomer contents. However, the molecular weights are not as high as it would be useful to give the polymer the desired properties. Besides, these molecular weights suddenly lower when the comonomer content increases, or when the polymerization temperature rises.

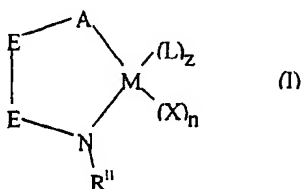
[0004] In EP 416815 and EP 420436 there is the description of a type of organometallic catalysts in which a transition metal is coordinated to a cyclopentadienyl ring and to a heteroatom. These organometallic compounds, when they are activated with alkylaluminoxanes, are able to produce ethylene polymers with high molecular weight and narrow distribution of molecular weight. They moreover own a great effectiveness in comonomer incorporation. However, when the comonomer content of the polymeric chain is increasing, the molecular weight sensibly decreases.

[0005] EP 416815 and Stevens, J.C. (Studies in surface science catalysis, Vol. 89, 1994, 277-84) disclose catalyst systems comprising a metallocene having constrained geometry, useful in the polymerization of addition polymerizable monomers, such as ethylenically unsaturated monomers. None of the compounds specifically disclosed in these references contains a bridge comprising a Si atom and a C atom.

[0006] Dias, H.V.R et al. (Journal of Organometallic Chemistry, Vol. 508, No. 1, 1996, 91-99) disclose compounds containing a fluorenyl group, such as 1-t-butyl-2-(9-fluorenyl)-1,1-dimethylsilaethanediyl)titanium, zirconium or hafnium dichloride, useful as catalyst precursors in olefin polymerization. However, Dias et al., does not provide with any indication on the possible results of said compounds in a polymerization process.

[0007] Therefore it is an object of the present invention to provide compounds, useful in the (co)polymerization of alpha-olefins, in particular in the (co)polymerization of ethylene, which can produce polymers with high molecular weights. Besides, these catalysts are specially efficient in the comonomer incorporation, and produce copolymers with totally random distributions of the comonomer.

[0008] The organo metallic complexes (catalysts) disclosed in the present invention are characterized by the following general formula I:



wherein:

M is a transition metal of groups 3, 4-10 of the periodic table of the elements, lanthanide or actinide, preferably titanium, zirconium or hafnium.

Each X group, equal to or different from each other, is hydrogen, halogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms, linear or branched, the hydrogens of these groups optionally are substituted by SiR₃, GeR₃, OR, NR₂, OSiR₃ groups or any combination thereof wherein R is selected from the group comprising: hydrogen, C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkenyl, C₇-C₂₀ arylalkyl, C₇-C₂₀ arylalkenyl or alkylaryl, branched or linear.

n is a number whose value is: 0, 1, 2 or 3, in order to fill the remaining free valences of the metal M;

L is a neutral Lewis base such as diethylether, tetrahydrofurane, dimethylaniline, aniline, triphenylphosphine, and n-butylamine

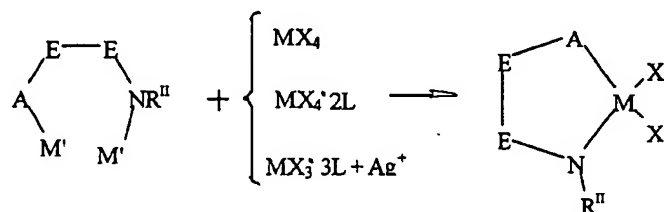
z is a number whose value is: 0, 1, 2 or 3.

[0009] A is a cyclopentadienyl type of ring of formula $C_5R^I_4$, wherein each R^I group, equal to or different from each other is hydrogen, C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkenyl, C_7 - C_{20} arylalkyl, C_7 - C_{20} arylalkenyl or alkylaryl, branched or linear, the hydrogens of these groups optionally are substituted by SiR_3 , GeR_3 , OR, NR_2 , $OSiR_3$ groups or any combination thereof wherein R is above defined; R^I is also selected from the group comprising SiR_3 , GeR_3 , OR, R_2N , $OSiR_3$ groups or any combination thereof. Two adjacent R^I optionally unite in order to form a saturated or unsaturated polycyclic cyclopentadienyl ring selected from the group consisting of indenyl, tetrahydroindenyl, and octahydrofluorenyl, optionally substituted with R^I groups.

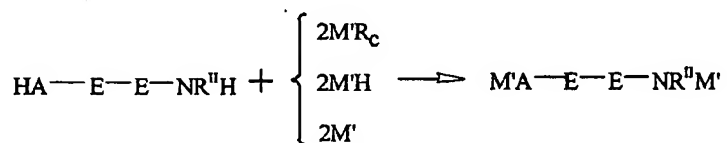
[0010] R^{II} is hydrogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl from 1 to 20 carbon atoms, linear or branched, whose hydrogens are optionally substituted by SiR_3 , GeR_3 , OR, NR_2 , $OSiR_3$ groups or any combination thereof wherein R is above defined; it optionally forms a condensed ring through another bond with E. Preferably R^{II} is tertbutyl.

[0011] The bridge E-E is $CR^{IV}_2-SiR^{III}_2$ or $SiR^{III}_2-CR^{IV}_2$. Each R^{III} , equal to or different from each other, is hydrogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms, linear or branched, whose hydrogens optionally are substituted by SiR_3 , GeR_3 , OR, NR_2 , $OSiR_3$ groups or any combination thereof wherein R is above defined; R^{IV} has the same meaning of R^{III} or it is halogen; besides two groups selected from R^{IV} and R^{III} belonging to different E optionally form a cyclic structure.

[0012] The catalysts component of general formula I, can be suitably prepared through reaction of a compound of general formula $M'-A-E-E-NR^{II}-M'$, wherein M' is Li, Na or K, with a metal M compound, preferably of formula MX_4 or with an adduct of formula $MX_4 \cdot 2L$ or $MX_3 \cdot 3L$, where X is above defined and L preferably is a linear or cyclic ether as for example: ethylic ether, tetrahydrofurane, dimethoxyethane, etc.



[0013] The compound of general formula $M'-A-E-E-NR^{II}-M'$ can be suitably prepared through reaction of $HA-E-E-NR^{II}H$ with two equivalents of an alkyl or aryl alkali metal salt, or with an alkali metal hydride or an alkaline metal:

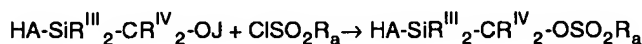


[0014] Wherein R_c is C_1 - C_{20} alkyl or C_6 - C_{20} aryl.

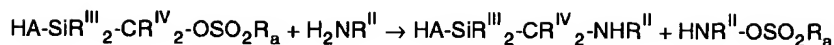
[0015] Alternatively, alkyl magnesium salts, which are obtained in the same way, can be used, but using an alkyl magnesium halide instead of alkyl lithium.

[0016] When the bridge E-E is $SiR^{III}_2-CR^{IV}_2$, the compound $HA-SiR^{III}_2-CR^{IV}_2-NR^{II}H$ can be suitably prepared starting from a compound of general formula $HA-SiR^{III}_2-CR^{IV}_2-OH$ or its lithium salts. The process comprises the following steps:

a) reacting a compound of formula $HA-SiR^{III}_2-CR^{IV}_2-OJ$ wherein J is lithium or hydrogen with an alkyl- or aryl-sulphonates according to the scheme:



b) contacting the recovered product of step a) with an excess of an amine of formula $NR^{II}H_2$



wherein R_a is $\text{C}_1\text{-C}_{20}$ alkyl, perfluoralkyl or $\text{C}_6\text{-C}_{20}$ aryl radical.

[0017] During the process for obtaining the intermediate compound of formula $\text{HA-E-E-NR}^{\text{II}}\text{H}$ and their alkali metal or magnesium halide salts, as well as the organometallic complexes obtained therefrom with the transition metal salts, the reaction temperature is kept between -100°C and 95°C , preferably between -80°C and 80°C , operating preferably under nitrogen inert atmosphere.

[0018] As non polar solvents pentane, hexane and toluene can be used; as polar aprotic solvents ethers such as diethyl ether, tetrahydrofurane or dimethoxyethane can be used.

[0019] During the whole process, both the chemical species and the solvents were protected from oxygen and humidity. The organometallic catalysts, when stored under inert atmosphere, are active in polymerization for long periods of time.

[0020] Non-limiting examples of compounds of general formula I are :

(1-*tert*butylamide-2-cyclopentadienyl-1,1-dimethylsilaethanediyl) titanium dichloride
 (1-*tert*butylamide-2-cyclopentadienyl-1,1-dimethylsilaethanediyl) zirconium dichloride
 (1-*tert*butylamide-2-cyclopentadienyl-1,1-dimethylsilaethanediyl) hafnium dichloride
 (1-*tert*butylamide-1,1-dimethylsilaethanediyl-2-(tetramethylcyclopentadienyl) titanium dichloride
 (1-*tert*butylamide-1,1-dimethylsilaethanediyl-2-(tetramethylcyclopentadienyl) zirconium dichloride
 (1-*tert*butylamide-2-(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane-diyl) titanium dichloride
 (1-*tert*butylamide-2-(tetramethylcyclopentadienyl)-1,1,2,2-tetramethyldisilane-diyl) zirconium dichloride
 (1-*tert*butylamide-2-(1-indenyl)-1,1-dimethylsilaethanediyl) titanium dichloride
 (1-*tert*butylamide-2-(1-indenyl)-1,1-dimethylsilaethanediyl) zirconium dichloride
 (1-*tert*butylamide-2-(1-indenyl)-1,1-dimethylsilaethanediyl) hafnium dichloride
 (1-*tert*butylamide-2-(1-indenyl)-1,1,2,2-tetramethylsilaethanediyl) titanium dichloride
 (1-*tert*butylamide-2-(1-indenyl)-1,1,2,2-tetramethylsilaethanediyl) zirconium dichloride
 (1-*tert*butylamide-2-(1-(2-methylindenyl)-1,1-dimethylsilaethanediyl) titanium dichloride
 (1-*tert*butylamide-2-(1-(2-methylindenyl)-1,1-dimethylsilaethanediyl) zirconium dichloride

The organometallic catalysts of formula I can be used in the polymerization and copolymerization of alpha-olefins through the addition of cocatalysts. These cocatalysts are compounds which can form non-coordinative anions, such as alkylaluminumoxanes or boron perfluorinated compounds. Representative, but non-limiting, examples are methylaluminoxane, ethylaluminoxane, dimethylanilinotetrakis(pentafluorophenyl)borane, and trispentafluorophenylborane. In case boron derivatives are used, it is preferable to add to the polymerization medium little quantities of aluminium alkyls (TIBA, TEA, and TMA).

The catalytic systems thus prepared are fit for the polymerization of alpha-olefins with 2 to 20 carbon atoms, in particular for the polymerization of ethylene, and for the copolymerization of ethylene with at least one alpha-olefin with 3 to 20 carbon atoms, such as propylene, 1-butene, 4-methyl-pentene, and 1-hexene with dienes, with cycloalkenes and with styrene. Preferably ethylene is copolymerized with propene, 1-butene, 1-hexene, 1-octene, 1-hexadecene, 4-methyl-pentene, hexadiene and styrene or mixtures thereof. The polymerization can be realized through a process in solution, in suspension, in gas phase or in bulk at high pressure and temperature. When using a process in suspension, hydrocarbon solvents, such as branched or linear aliphatic hydrocarbons (hexane, heptane, isobutane, etc.), cyclic hydrocarbons (benzene, toluene, xylene, etc.) or a mixture thereof are used as reaction medium. The polymerization can be realized between 1 and 4000 atmospheres and temperatures between -60 and 300°C , preferably between -40 and 220°C , and the polymerization time can vary between 20 seconds and 6 hours, according to the process.

The used concentration of the organometallic catalyst, is from 10^{-7} to 10^{-3} M, preferably from 10^{-6} to 10^{-4} M. The organoaluminum compound (for example an aluminoxane) is used in a concentration from 10^{-4} to 10^{-1} M, preferably from 10^{-3} to 10^{-2} M. However, bigger concentrations of both components are possible as well. When an aluminoxane is used as a cocatalyst, the used Al/M molar ratio ranges from 100 to 10000, preferably between 500 and 1500. When a boron compound is used, the molar ratio varies in the range 0.5-10, preferably between 0.9-5.

The molecular weight of the obtained polymers can be controlled by varying the concentration of catalyst, cocatalyst and monomer in the polymerization medium, by varying the polymerization temperature as well as by the addition of regulators of the molecular weight such as H_2 . When in the preparation of the catalyst only one type of cocatalyst is used, polymers with narrow distributions of the molecular weight are obtained. However, when several types of catalysts and/or cocatalysts are used, the obtained polymers have broad distribution of molecular weight, including also multimodal distributions.

The copolymerization reactions can be realized by using the same process as the one used in the homopolymerization process, but moreover by feeding the reaction medium with the suitable comonomer or comonomers. The preferred comonomer/monomer molar ratio is comprised between 0.1/1 and 5/1. In this way, copolymers with controlled content and random distribution of comonomer are obtained.

Figure 1 shows some examples of compounds of formula I.

The following examples are described in order to better understand the invention. The materials, the chemical compounds and the conditions used in these examples are illustrative and do not limit the scope of the invention.

The average molecular weights in number, weight and distribution were determined through gel permeation chromatography GPC or SEC. The intrinsic viscosities $[\eta]$ were obtained at 145°C through viscosimetric techniques, using as a solvent trichlorobenzene with 0.05% of antioxidant in order to prevent polymer degradation.

EXAMPLE 1

a) Preparation of 2-bromo-1-*tert*-butylamino-1,1-dimethylsilaethane

[0021] A solution of 13.5 g (72 mmol) of 2-bromo-1-chloro-1,1-dimethylsilaethane was prepared, 21 g (288 mmol) of *tert*-butylamine was added dropwise, the formation of a whitish solid was immediately observed. The reaction was continued for 12 hours, then it was brought to dryness and the resulting pasty solid was extracted with hexane, the obtained solution was brought to dryness in order to obtain a yellow oil. (14.5 g, 64.7 mmol, yield: 90%). $^1\text{H-NMR}$ (CDCl_3): 2.45(s,2H), 1.09(s,9H), 0.15(s,6H).

b) Preparation of 1-*tert*-butylamino-2-cyclopentadienyl-1,1-dimethylsilaethane

[0022] 32.7 ml of a 2.3 M solution (75 mmol) of sodium cyclopentadienide in tetrahydrofuran was added to a solution of 11.4 g (51 mmol) of 2-bromo-1-*tert*-butylamino-1,1-dimethylsilaethane. The immediate formation of a pinkish solid was observed, the reaction was continued for 8 hours, then it was concentrated to dryness and it was extracted with hexane, the resulting solution was evaporated in order to give a yellow oil, that corresponds to a mixture of isomers (12.5 g, 60 mmol, yield: 80%). $^1\text{H-NMR}$ (CDCl_3): 6.5-5.75(m,3H), 2.95(m,2H), 1.90(m,2H), 1.20(s,9H), 0.10(s,6H).

c) Preparation of the dilithium salt of 1-*tert*-butylamino-2-cyclopentadienyl-1,1-dimethylsilaethane

[0023] 11.4 ml of 2.5 M solution (28.6 mmol) of butyl lithium in hexane was added to a solution of 3 g (14.3 mmol) of 1-*tert*-butylamino-2-cyclopentadienyl-1,1-dimethylsilaethane in ether at -78°C. It was maintained under stirring for 4 hours, at the end it was concentrated to dryness, producing a whitish solid, which was twice washed with hexane (1.7 g, 7.7 mmol, yield: 54%).

d) Preparation of (1-*tert*-butylamino-2-cyclopentadienyl-1,1-dimethylsilaethanediyl) titanium dichloride

[0024] A suspension of 3.42 g (15.5 mmol) of the dilithium salt of 1-*tert*-butylamino-2-cyclopentadienyl-1,1-dimethylsilaethane in toluene was prepared and it was added to a suspension of 5.17 g (15.5 mmol) of titanium tetrachloride mixed with tetrahydrofuran in toluene at -78°C. The formation of a greenish solid was immediately observed, the reaction was left under stirring for 12 hours, the solution was filtered, obtaining a brown solution which was concentrated in order to give a brown solid, which was recrystallized in hexane (2.3 g, 7.1 mmol, yield: 46%). $^1\text{H-NMR}$ (C_6D_6): 6.42(m,3H), 5.81(m,3H), 1.82(s,2H), 1.60(s,9H).

EXAMPLE 2

a) Preparation of (1-*tert*-butylamino-2-cyclopentadienyl-1,1-dimethylsilaethanediyl) zirconium dichloride

[0025] A suspension of 1.46 g (6.3 mmol) of zirconium tetrachloride in toluene was prepared and a suspension of 1.4 g (6.3 mmol) of the dilithium salt of 1-*tert*-butylamino-2-cyclopentadienyl-1,1-dimethylsilaethane in toluene was added. A greenish suspension immediately was formed and it was left under stirring for 12 hours. The suspension was settled, filtered and concentrated, obtaining a yellow compound: (0.74 g, 2.0 mmol, yield: 32%) $^1\text{H-NMR}$ (C_6D_6): 6.22(m,2H), 5.81(m,2H), 1.73(s,2H), 1.54(s,9H).

EXAMPLE 3

a) Preparation of 1-*tert*butylamino-2-(1-indenyl)-1,1-dimethylsilaethane

[0026] A 20 g (182 mmol) solution of indenyl lithium in tetrahydrofuran was added to a solution of 41 g (182 mmol) of 2-bromo-1-*tert*butylamino-1,1-dimethylsilaethane at 0°C. After the reaction was concentrated to dryness and the residue was extracted with hexane. Finally, the solution in hexane was concentrated to the obtainment of an orange oil: 13.5 g (52 mmol, yield: 29%). ¹H-NMR (CDCl₃): 7.50(m,1H), 7.39(m,1H), 7.35(m,1H), 7.23(m,1H), 6.17(m,1H), 3.42(m,2H), 2.17(m,2H), 1.22(m,9H), 0.20(m,6H).

b) Preparation of the dilithium salt of 1-*tert*butylamino-2-(1-indenyl)-1,1-dimethylsilaethane.

[0027] 17.3 ml of a 2.5 M (43.2 mmol) solution of butyllithium in hexane was added to a 5.6 g (21.6 mmol) solution of 1-*tert*butylamino-2-(1-indenyl)-1,1-dimethylsilaethane in ether at -78°C. The butane evolution was immediately observed and, when room temperature was achieved, it was maintained under stirring for 2 hours, then it concentrates to dryness and the resulting solid was twice washed with hexane in order to give a yellowish powdery solid: 5.8 g (21 mmol, yield: 97%).

c) Preparation of [1-*tert*butylamide-2-(1-indenyl)-1,1-dimethylsilaethanediyl] titanium dichloride

[0028] A suspension of 5.8 g (21 mmol) of the dilithium salt of 1-*tert*butylamino-2-(1-indenyl)-1,1-dimethylsilaethane in ether was added to a suspension of 4.1 g (21.6 mmol) of titanium tetrachloride in ether at -78°C. A brown suspension immediately was formed and maintained under stirring at room temperature for 12 hours. The resulting suspension was brought to dryness and it was extracted several times with hexane, obtaining a red solution and concentrating it a dark-brown solid was formed: 2.5 g (6.7 mmol, yield: 32%). ¹H-NMR (CDCl₃): 7.67(m,1H), 7.56(m,1H), 7.32(m,2H), 6.88(m,1H), 6.55(m,1H), 2.79(m,1H), 2.55(m,1H), 1.55(s,9H), 0.62(s,3H), 0.61(s,3H). ¹³C-NMR (CDCl₃): 130.9, 128.2, 128.0, 127.3, 126.8, 126.1, 123.4, 118.4, 112.3, 63.7, 32.8, 18.4, 7.7, 6.2.

EXAMPLE 4

a) Preparation of [1-*tert*butylamide-2-(1-indenyl)-1,1-dimethylsilaethanediyl] zirconium dichloride

[0029] A suspension of 5.0 g (18.5 mmol) of the dilithium salt of 1-*tert*butylamino-2-(1-indenyl)-1,1-dimethylsilaethane in ether was added to a suspension of 4.3 g (18.5 mmol) of zirconium tetrachloride in ether at -78°C. A yellowish suspension immediately forms and it was maintained under stirring at room temperature for 12 hours. The resulting suspension was brought to dryness and it was extracted several times with toluene, obtaining a yellowish solution, when concentrated it produced a yellow solid: 2.1 g (5 mmol, yield: 27%). ¹H-NMR (CDCl₃): 7.60(m,2H), 7.28(m,2H), 6.68(m,1H), 6.48(m,1H), 2.57(m,1H), 2.38(m,1H), 1.50(s,9H), 0.57(s,3H), 0.62(s,3H), 0.48(s,3H). ¹³C-NMR (CDCl₃): 128.0, 126.8, 126.3, 126.0, 125.3, 122.3, 122.0, 117.0, 103.5, 56.6, 32.6, 16.7, 7.2, 6.3.

EXAMPLE 5

[0030] To a glass reactor of 1 liter, previously dried and outgassed, 600 ml of n-heptane was added. The temperature was raised to 70°C and the solvent was stirred at 1200 rpm. When the thermal equilibrium was achieved, the medium was saturated with ethylene at a pressure of 4 bar. 10 ml of a MAO solution in toluene (1.5 M in total aluminium) and 2 bar of ethylene was added. The pressure was raised to 4 bar and 2 minutes later 0.01 mmol of the organometallic compound described in example 3 was added. The system was fed with ethylene for 15 minutes and then the polymerization was stopped by closing the ethylene flux and adding 20 ml of acidified methanol. 0.86 g of polyethylene was obtained.

EXAMPLE 6

[0031] Ethylene and 1-hexene were copolymerized. For that, the identical method as in the previous example was used, but once the solvent had been added and before pressurizing the reactor, 8 ml of dry and just-distilled 1-hexene were injected. 10 ml of a MAO solution in toluene (1.5 M in total aluminium) and 0.01 mmol of the organometallic compound described in example 3 in toluene were used. After 15 minutes of polymerization 1.4 g of polyethylene was obtained with M_w 198,400 and 0.7% by mol of 1-hexene distributed at random.

EXAMPLE 7

[0032] Ethylene and 1-hexene were copolymerized. For that, the identical method as in the example 5 was used, but once the solvent had been added and before pressurizing the reactor, 25 ml of dry and just-distilled 1-hexene were injected. 10 ml of a MAO solution in toluene (1.5 M in total aluminium) and 0.01 mmol of the organometallic compound described in example 3 in toluene were used. After 15 minutes of polymerization 0.42 g of polyethylene was obtained with M_w 279,000 and 1.15% by mol of 1-hexene distributed at random.

EXAMPLE 8

[0033] To a glass reactor of 1 liter, previously dried and outgassed, 600 ml of n-heptane and 8 ml of dry and just-distilled 1-hexene were added. The temperature was raised to 70°C and the solvent was stirred at 1200 rpm. When the thermal equilibrium was achieved, the medium was saturated with ethylene at a pressure of 4 bar. 10 ml of a MAO solution in toluene (1.5 M in total aluminium) and 2 bar of ethylene was added. The pressure was raised to 4 bar and 2 minutes later 0.01 mmol of the organometallic compound described in example 4 was added. The system was fed with ethylene for 15 minutes and then the polymerization was stopped by closing the ethylene flux and adding 20 ml of acidified methanol. 5.4 g of polyethylene was obtained with M_w 340,796 and 0.7% by mol of 1-hexene distributed at random.

EXAMPLE 9

[0034] Ethylene and 1-hexene were copolymerized. For that, the identical method as in the example 8 was used, but once the solvent had been added and before pressurizing the reactor, 25 ml of dry and just-distilled 1-hexene were injected. 10 ml of a MAO solution in toluene (1.5 M in total aluminium) and 0.01 mmol of the organometallic compound described in example 4 in toluene were used. After 15 minutes of polymerization 5.6 g of polyethylene was obtained with M_w 262,678 and 1.43% by mol of 1-hexene distributed at random.

EXAMPLE 10

[0035] To a glass reactor of 1 liter, previously dried and outgassed, 600 ml of n-heptane and 8 ml of dry and just-distilled 1-hexene were added. The temperature was raised to 70°C and the solvent was stirred at 1200 rpm. When the thermal equilibrium was achieved, the medium was saturated with ethylene at a pressure of 4 bar. 10 ml of a MAO solution in toluene (1.5 M in total aluminium) and 2 bar of ethylene was added. The pressure was raised to 4 bar and 2 minutes later 0.01 mmol of the organometallic compound described in example 2 was added. The system was fed with ethylene for 15 minutes and then the polymerization was stopped by closing the ethylene flux and adding 20 ml of acidified methanol. 1.9 g of polyethylene was obtained with M_w 567066 and 0.65% by mol of 1-hexene distributed at random.

EXAMPLE 11

[0036] To a glass reactor of 1 liter, previously dried and outgassed, 600 ml of n-heptane and 8 ml of dry and just-distilled 1-hexene were added. The temperature was raised to 70°C and the solvent was stirred at 1200 rpm. When the thermal equilibrium was achieved, the medium was saturated with ethylene at a pressure of 4 bar. 10 ml of a MAO solution in toluene (1.5 M in total aluminium) and 2 bar of ethylene was added. The pressure was raised to 4 bar and 2 minutes later 0.01 mmol of the organometallic compound described in example 1 was added. The system was fed with ethylene for 15 minutes and then the polymerization was stopped by closing the ethylene flux and adding 20 ml of acidified methanol. 8.3 g of polyethylene was obtained with M_w 69,470 and 0.2% content of 1-hexene distributed at random.

EXAMPLE 12

[0037] Ethylene and 1-hexene were copolymerized. For that, the identical method as in the example 11 was used, but once the solvent had been added and before pressurizing the reactor, 25 ml of dry and just-distilled 1-hexene were injected. 10 ml of a MAO solution in toluene (1.5 M in total aluminium) and 0.01 mmol of the organometallic compound described in example 1 in toluene were used. After 15 minutes of polymerization 9.3 g of polyethylene was obtained with M_w 68,920 and 0.6% by mol of 1-hexene distributed at random.

EXAMPLE 13

a) Preparation of 1-*tert*butylamino-1,1-dimethyl-2-tetramethylcyclopentadienyl silaethane

[0038] A solution of 13 g (82 mmol) potassium tetramethylcyclopentadienide in tetrahydrofuran was added to a solution of 18.4 g (82 mmol) of 2-bromo-1-*tert*butylamino-1,1-dimethylsilaethane. The immediate formation of a pinkish solid was observed, the reaction was continued for 8 hours at reflux temperature, then it was concentrated to dryness and it was extracted with hexane, the resulting solution was evaporated in order to give a orange oil (9.8 g, 37.0 mmol, yield: 45%). $^1\text{H-NMR}$ (CDCl_3): 2.5(m,1H), 1.9(s,6H), 1.85(s,6H), 1.12(s,9H), 1.00(m,2H), 0.10(s,6H).

b) Preparation of the dilithium salt of 1-*tert*butylamino-1,1-dimethyl-2-tetramethylcyclopentadienyl silaethane

[0039] 11.2 ml of 2.5 M solution (28 mmol) of butyllithium in hexane was added to a solution of 3.6 g (14 mmol) of 1-*tert*butylamino-1,1-dimethyl-2-tetramethylcyclopentadienyl silaethane in ether at -78°C . It was maintained under stirring for 4 hours, at the end it was concentrated to dryness, producing a whitish solid, which was twice washed with hexane (3.3 g, 11.2 mmol, yield: 80%).

c) Preparation of [1-*tert*butylamine-1,1-dimethyl-2-tetramethylcyclopentadienylsilaethane] titanium dichloride

[0040] A suspension of 2.5 g (9 mmol) of the dilithium salt of 1-*tert*butylamino-1,1-dimethyl-2-tetramethylcyclopentadienyl silaethane in ether was prepared and it was added to a suspension of 1.7 g (9 mmol) of titanium tetrachloride in ether at -78°C . The formation of a brownish solid was immediately observed, the reaction was left under stirring for 12 hours, the suspension was concentrated in order to give a brown oily-solid, which was recrystallized in hexane to give a red microcrystalline solid (1.3 g, 3.4 mmol, yield: 46%). $^1\text{H-NMR}$ (C_6D_6): 2.30(s,2H), 2.27(s,6H), 2.22(s,6H), 1.60(s,9H), 0.50(s,6H).

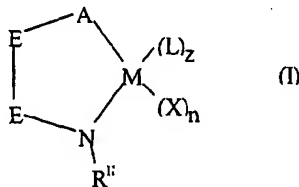
EXAMPLE 14

Preparation of [1-*tert*butylamino-1,1-dimethyl-2-tetramethylcyclopentadienylsilaethane] zirconium dichloride

[0041] A suspension of 3.88 g (14 mmol) of the dilithium salt of 1-*tert*butylamino-1,1-dimethyl-2-tetramethylcyclopentadienyl silaethane in ether was prepared and it was added to a suspension of 3.3 g (14 mmol) of zirconium tetrachloride in ether at -78°C . The formation of a yellowish suspension was immediately observed, the reaction was left under stirring for 12 hours, the suspension was concentrated in order to give a yellow oily-solid, which was recrystallized in hexane to give a yellow microcrystalline solid (2.3 g, 5.4 mmol, yield: 39%). $^1\text{H-NMR}$ (C_6D_6): 2.20(s,6H), 2.13(s,6H), 2.12(s,2H), 1.62(s,9H), 0.42(s,6H).

Claims

1. Catalyst component for the polymerization of α -olefins of general formula (I)



wherein:

M is a transition metal of groups 3, 4-10 of the periodic table of the elements, lanthanide or actinide; each X group, equal to or different from each other, is hydrogen, halogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms, linear or branched, the hydrogens of these groups are optionally substituted by SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 groups or any combination thereof wherein R is selected from the group comprising: hydrogen, C_1 - C_{20} alkyl, C_3 - C_{20} cycloalkyl, C_6 - C_{20} aryl, C_7 - C_{20} alkenyl,

C_7-C_{20} arylalkyl, C_7-C_{20} arylalkenyl or alkylaryl, branched or linear;

n is a number whose value is: 0, 1, 2 or 3, in order to fill the remaining free valences of the metal M; L is a neutral Lewis base;

z is a number whose value is: 0, 1, 2 or 3;

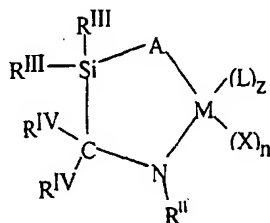
A is a cyclopentadienyl type of ring of formula $C_5R^I_4$, wherein each R^I group, equal to or different from each other is hydrogen, C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkenyl, C_7-C_{20} arylalkyl, C_7-C_{20} arylalkenyl or alkylaryl, branched or linear; the hydrogens of these groups optionally are substituted by SiR_3 , GeR_3 , OR, NR_2 , $OSiR_3$ groups or any combination thereof wherein R is above defined; R^I is also selected from the group comprising SiR_3 , GeR_3 , OR, NR_2 , $OSiR_3$ groups or any combination thereof; two adjacent R^I optionally unite in order to form a saturated or unsaturated polycyclic cyclopentadienyl ring selected from the group consisting of indenyl, tetrahydroindenyl, and octahydrofluorenyl, optionally substituted with R^I groups; R^{II} is hydrogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl from 1 to 20 carbon atoms, linear or branched, whose hydrogens optionally are substituted by SiR_3 , GeR_3 , OR, NR_2 , $OSiR_3$ groups or any combination thereof wherein R is above defined; it optionally forms a condensed ring through another bond with E;

E-E is $CR^{IV}_2-SiR^{III}_2$ or $SiR^{III}_2-CR^{IV}_2$; each R^{III} , equal to or different from each other, is hydrogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms, linear or branched, where hydrogens optionally are substituted by SiR_3 , GeR_3 , OR, NR_2 , $OSiR_3$ groups or any combination thereof wherein R is above defined; R^{IV} has the same meaning of R^{III} or it is halogen; besides two group selected from R^{IV} and R^{III} belonging to different E optionally form a cyclic structure.

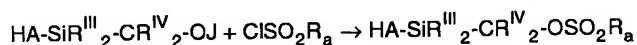
2. Catalyst component according to claim 1 wherein, in general formula (I) M is selected from the group consisting of zirconium, titanium or hafnium.
3. Catalyst component according to claim 1 wherein the bridging group E-E is $CR^{IV}_2-SiR^{III}_2$.
4. Catalyst component according to claims 1-3 wherein R^{II} is tertbutyl.
5. Catalyst system comprising a cocatalyst selected from the group consisting of: alkylaluminoxane, modified aluminoxane and boron compound, and a catalyst component according to claims 1-4.
6. Catalyst system according to claim 5 wherein, the cocatalyst is selected from the group comprising: methylaluminoxane, ethylaluminoxane, N,N-dimethylanilinium tetrakis (pentafluorophenyl)borate, and tris(pentafluorophenyl)borane.
7. Process for obtaining polyolefins in solution, in suspension, in gas phase at low and high pressures and temperatures or in mass at high pressure and high or low temperature, wherein the temperature varies between -60°C and 300°C , the pressure varies between 1 and 4000 atmospheres, comprising the use of the catalyst system according to claims 5-6.
8. Process for obtaining polyolefins according to claim 7, wherein the polymerization temperature varies between -60°C and 300°C , the pressure varies between 1 and 4000 atmospheres, the transition metal concentration varies between 10^{-7} and 10^{-3} M, the cocatalyst is an aluminium organocomplex and the cocatalyst/transition metal molar ratio varies between 10 and 10000.
9. Process for obtaining polyolefins according to claim 8, wherein the polymerization temperature varies between -40°C and 220°C , the transition metal concentration varies between 10^{-6} and 10^{-4} M, the cocatalyst is an aluminium organocomplex and the cocatalyst/transition metal molar ratio varies between 500 and 1500.
10. Process for obtaining polyolefins according to claim 7, wherein the transition metal molar concentration varies between 10^{-7} and 10^{-3} , the cocatalyst is a boron compound and the cocatalyst/transition metal molar ratio varies between 0.5 and 10.
11. Process for obtaining polyolefins according to claim 10, wherein the polymerization temperature varies between -40°C and 220°C , the transition metal concentration varies between 10^{-6} and 10^{-4} M, the cocatalyst is a boron compound and the cocatalyst/transition metal molar ratio varies between 0.9 and 5.
12. Process for obtaining polyolefins according to claims 8-11, wherein the monomer is ethylene.

13. Process for obtaining ethylene copolymers according to claim 8-12, wherein the comonomer is selected from the group comprising: propene, 1-butene, 1-hexene, 1-octene, 1-hexadecene, 4-methyl-pentene, hexadiene and styrene or mixtures thereof.

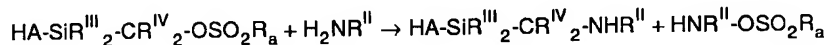
5 14. Process for obtaining a compound of formula:



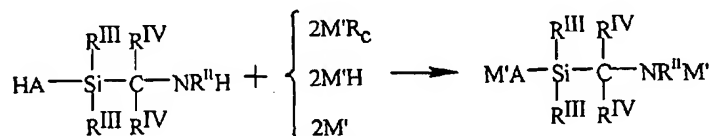
wherein A, E, M, L, X, n, z, R^{II}, R^{III} and R^{IV} are defined in claims 1-5 characterized by the following steps reacting a compound of formula HA-SiR^{III}₂-CR^{IV}₂-OJ wherein J is lithium or hydrogen with an alkyl- or aryl-sulphonates according to the scheme:



contacting the recovered product of step a) with an excess of an amine of formula NR^{II}H₂



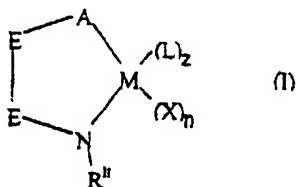
wherein R_a is C₁-C₂₀ alkyl, perfluoroalkyl or C₆-C₂₀ aryl radical treating the compound of formula HA-SiR^{III}₂-CR^{IV}₂-NHR^{II} with two equivalents of an alkyl or aryl alkali metal salt, or with an alkali metal hydride or an alkali metal according to the following scheme:



wherein R_c is C₁-C₂₀ alkyl or C₆-C₂₀ aryl and M' is selected from the group comprised: Li, Na and K contacting the compound of formula M'A-SiR^{III}₂-CR^{IV}₂-NR^{II}M' with a metal M compound, of formula MX₄ or with an adduct of formula MX₄2L, or MX₃3L, wherein L is a linear or cyclic ether.

Patentansprüche

1. Katalysatorkomponente für die Polymerisation von Alpha-Olefinen der allgemeinen Formel (I)



in welcher:

M ein Übergangsmetall aus den Gruppen 3 oder 4-10 der Tabelle des periodischen Systems der Elemente, Lanthanoide oder Actinide ist;

jede Gruppe X, die gleich oder voneinander verschieden sein können, geradliniger oder verzweigter Wasserstoff, Halogen, Alkyl, Cycloalkyl, Aryl, Alkenyl, Arylalkyl, Arylalkenyl oder Alkylaryl mit 1 bis 20 Kohlenstoff ist, wobei die Wasserstoffe dieser Gruppen wahlweise durch SiR_3 -, GeR_3 -, OR -, NR_2 -, OSiR_3 -Gruppen oder eine beliebige Kombination derselben ersetzt sind, wobei R aus der aus geradlinigem oder verzweigtem Wasserstoff, C_1 - C_{20} -Alkyl, C_3 - C_{20} -Cycloalkyl, C_6 - C_{20} -Aryl, C_7 - C_{20} -Alkenyl, C_7 - C_{20} -Arylalkyl, C_7 - C_{20} -Arylalkenyl oder Alkylaryl bestehenden Gruppe ausgewählt ist;

n eine Zahl mit dem Wert von: 0, 1, 2 oder 3 zum Ausfüllen der freien Wertigkeiten des Metalls M ist;

L eine neutrale Lewis-Base ist;

z eine Zahl mit dem Wert von: 0, 1, 2 oder 3 ist;

A ein Ring vom Typ Cyclopentadienyl der Formel C_5R^1_4 ist, in welcher jede R^1 -Gruppe, die gleich oder voneinander verschieden sein können, geradliniger oder verzweigter Wasserstoff, C_1 - C_{20} -Alkyl, C_3 - C_{20} -Cycloalkyl, C_6 - C_{20} -Aryl, C_7 - C_{20} -Alkenyl, C_7 - C_{20} -Arylalkyl, C_7 - C_{20} -Arylalkenyl oder Alkylaryl ist; wobei die Wasserstoffe dieser Gruppen wahlweise durch SiR_3 -, GeR_3 -, OR -, NR_2 -, OSiR_3 oder eine beliebige Kombination derselben ersetzt sind, und R wie oben angegeben ist; wobei R^1 ebenfalls aus der Gruppe aus SiR_3 -, GeR_3 -, OR -, NR_2 -, OSiR_3 oder einer beliebigen Kombination derselben ausgewählt ist;

wobei wahlweise zwei benachbarte R^1 unter Ausbildung eines polyzyklischen gesättigten oder ungesättigten, aus der aus Indenyl, Tetrahydroindenyl und Octahydrofluorenyl zusammengesetzten Gruppe ausgewählten, wahlweise durch R^1 -Gruppen ersetzen Cyclopentadienylrings verbunden werden;

R^{11} geradliniger oder verzweigter Wasserstoff, Alkyl, Cycloalkyl, Aryl, Alkenyl, Arylalkyl, Arylalkenyl oder Alkylaryl mit 1 bis 20 Kohlenstoffatomen ist, deren Wasserstoffe wahlweise durch SiR_3 -, GeR_3 -, OR -, NR_2 -, OSiR_3 -Gruppen oder eine beliebige Kombination derselben ersetzt sind und R wie oben angegeben ist; wobei wahlweise ein kondensierter Ring durch eine weitere Verbindung mit E gebildet wird;

E-E $\text{CR}^{\text{IV}}_2\text{-SiR}^{\text{III}}_2$ oder $\text{SiR}^{\text{III}}_2\text{-CR}^{\text{IV}}_2$ ist; jedes R^{III} , die gleich oder voneinander verschieden sein können, geradliniger oder verzweigter Wasserstoff, Alkyl, Cycloalkyl, Aryl, Alkenyl, Arylalkyl, Arylalkenyl oder Alkylaryl mit 1 bis 20 Kohlenstoffatomen ist, wobei die Wasserstoffe wahlweise durch SiR_3 -, GeR_3 -, OR -, NR_2 -, OSiR_3 -Gruppen oder eine beliebige Kombination derselben ersetzt sind und R wie oben angegeben ist; R^{IV} die selbe Bedeutung wie R^{III} hat oder ein Halogen ist; und ausserdem die beiden aus R^{IV} und R^{III} ausgewählten, zu unterschiedlichen E gehörenden Gruppen wahlweise eine zyklische Struktur bilden.

2. Katalysatorkomponente gemäss Anspruch 1, bei deren allgemeinen Formel (I) M aus der aus Zirkonium, Titanium oder Hafnium bestehenden Gruppe ausgewählt ist.

3. Katalysatorkomponente gemäss Anspruch 1, bei welcher die Verbindungsgruppe E-E $\text{CR}^{\text{IV}}_2\text{-SiR}^{\text{III}}_2$ ist.

4. Katalysatorkomponente gemäss den Ansprüchen 1-3, bei welcher R^{II} tert.-Butyl ist.

5. Ein einen aus der aus Alkylaluminoxan, modifiziertem Aluminoxan und Borverbindung bestehenden Gruppe ausgewählten Cokatalysator enthaltendes Katalysatorsystem, sowie eine Katalysatorkomponente gemäss den Ansprüchen 1-4.

6. Katalysatorsystem gemäss Anspruch 5, bei welchem der Cokatalysator aus der aus Methylaluminoxan, Ethylaluminoxan, N,N-Dimethylanilin-Tetrakis(pentafluorphenyl)borat und Trispentafluorphenylboran bestehenden Gruppe ausgewählt ist.

7. Verfahren zur Herstellung von in Lösung, in Suspension, in Gasphase befindlichen Polyolefinen bei niedrigen und hohen Drücken und Temperaturen oder in Masse bei hohem Druck und hoher oder niedriger Temperatur, wobei die Temperatur zwischen -60°C und 300°C und der Druck zwischen 1 und 4000 atm. liegt, welches die Verwendung eines Katalysatorsystems gemäss den Ansprüchen 5-6 beinhaltet.

8. Verfahren zur Herstellung von Polyolefinen gemäss Anspruch 7, bei welchem die Polymerisationstemperatur zwischen -60°C und 300°C , der Druck zwischen 1 und 4000 atm und die Übergangsmetallkonzentration zwischen 10^{-7} und 10^{-3} M liegt, der Cokatalysator ein organischer Aluminiumkomplex ist und das Molverhältnis zwischen Cokatalysator / Übergangsmetall zwischen 10 und 10000 liegt.

9. Verfahren zur Herstellung von Polyolefinen gemäss Anspruch 8, bei welchem die Polymerisationstemperatur zwischen -40°C und 220°C und die Übergangsmetallkonzentration zwischen 10^{-6} und 10^{-4} M liegt, der Cokatalysator

ein organischer Aluminiumkomplex ist und das Molverhältnis zwischen Cokatalysator / Übergangsmetall zwischen 500 und 1500 liegt.

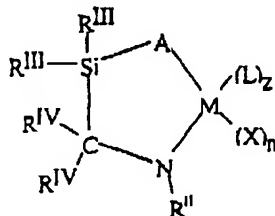
10. Verfahren zur Herstellung von Polyolefinen gemäss Anspruch 7, bei welchem die Übergangsmetallkonzentration zwischen 10^{-7} und 10^{-3} M liegt, der Cokatalysator ein Borkomplex ist und das Molverhältnis zwischen Cokatalysator / Übergangsmetall zwischen 0,5 und 10 liegt.

11. Verfahren zur Herstellung von Polyolefinen gemäss Anspruch 10, bei welchem die Polymerisationstemperatur zwischen -40°C und 220°C und die Übergangsmetallkonzentration zwischen 10^{-6} und 10^{-4} M liegt, der Cokatalysator ein Borkomplex ist und das Molverhältnis zwischen Cokatalysator / Übergangsmetall zwischen 0,9 und 5 liegt.

12. Verfahren zur Herstellung von Polyolefinen gemäss den Ansprüchen 8-11, bei welchem das Monomer Ethylen ist.

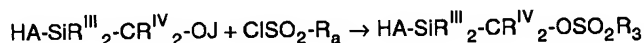
13. Verfahren zur Herstellung von Ethylenpolyolefinen gemäss Anspruch 8-12, bei welchem das Comonomer aus der Gruppe aus: Propen, 1-Buten, 1-Hexen, 1-Okten, 1-Hexadecen, 4-Methyl-Penten, Hexadiol und Styrol oder Mischungen derselben ausgewählt ist.

14. Verfahren zur Herstellung einer Verbindung der Formel:



In welcher A, E, M, L, X, n, z, R^{II}, R^{III} und R^{IV} wie in den Ansprüchen 1-5 sind, gekennzeichnet durch die folgenden Stufen:

Die Umsetzung einer Verbindung der Formel $\text{HA-SiR}^{\text{III}}_2\text{-CR}^{\text{IV}}_2\text{-OJ}$, in welcher J Lithium oder Wasserstoff ist, mit einem Alkyl- oder Arylsulfonat gemäss dem Schema:

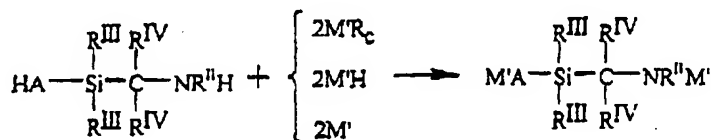


das in Kontakt bringen eines aus der Stufe a) gewonnenen Produktes mit einem Überschuss eines Amins der Formel $\text{NR}^{\text{II}}\text{H}_2$



in welcher R_a ein C₁-C₂₀-Alkylradikal, Perfluoralkyl oder C₆-C₂₀-Aryl ist;

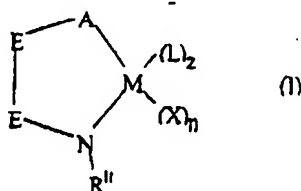
die Behandlung der Verbindung der Formel $\text{HA-SiR}^{\text{III}}_2\text{-CR}^{\text{IV}}_2\text{-NHR}^{\text{II}}$ mit zwei Äquivalenten eines Alkyl- oder Arylalkalimetallsalzes oder mit einem Alkalimetallhydrid oder einem Alkalimetall gemäss folgendem Schema:



bei welchem R_c C₁-C₂₀-Alkyl oder C₆-C₂₀-Aryl ist und M' aus der Gruppe aus: Li, Na und K ausgewählt ist; und das in Kontakt bringen der Verbindung der Formel $\text{M}^{\text{A}}\text{-SiR}^{\text{III}}_2\text{-CR}^{\text{IV}}_2\text{-NR}^{\text{II}}\text{M}^{\text{I}}$ mit einer Metallverbindung M der Form MX_4 , oder mit einem Addukt der Formel $\text{MX}_4\text{2L}$ oder $\text{MX}_3\text{3L}$, in welcher L ein geradliniger oder verzweigter Äther ist.

Revendications

1. Composant de catalyseur pour la polymérisation d'alpha-oléfines de formule générale (I)



dans laquelle :

M est un métal de transition des groupes 3 ou 4-10 de la table périodique des éléments, lanthanides ou actinides;

chaque groupe X, pouvant être égaux ou différents, est hydrogène, halogène, alcoyle, cycloalcoyle, aryle, alkényle, arylalcoyle, arylalkényle ou alkylaryle avec de 1 à 20 atomes de carbone, linéaire ou ramifié, les hydrogènes de ces groupes étant éventuellement remplacés par les groupes SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 ou n'importe quelle autre combinaison d'eux-mêmes, où R est sélectionné parmi le groupe composé de: hydrogène, alcoyle $\text{C}_1\text{-C}_{20}$, cycloalcoyle $\text{C}_3\text{-C}_{20}$, aryle $\text{C}_6\text{-C}_{20}$, alkényle $\text{C}_7\text{-C}_{20}$, arylalcoyle $\text{C}_7\text{-C}_{20}$, arylalkényle $\text{C}_7\text{-C}_{20}$ ou alkylaryle, linéaire ou ramifié;

n est un numéro dont la valeur est: 0, 1, 2 ou 3, pour remplir les valences libres restantes du métal M;

L est une base de Lewis neutre;

z est un numéro dont la valeur: 0, 1, 2 ou 3;

A est un anneau de type cyclopentadiénol de formule C_5R^1_4 , dans laquelle chaque groupe R^1 , pouvant être égaux ou différents, est hydrogène, alcoyle $\text{C}_1\text{-C}_{20}$, cycloalcoyle $\text{C}_3\text{-C}_{20}$, aryle $\text{C}_6\text{-C}_{20}$, alkényle $\text{C}_7\text{-C}_{20}$, arylalcoyle $\text{C}_7\text{-C}_{20}$, arylalkényle $\text{C}_7\text{-C}_{20}$ ou alkylaryle, linéaire ou ramifié; les hydrogènes de ces groupes étant éventuellement remplacés par SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 ou n'importe quelle autre combinaison d'eux-mêmes, où R est comme il a été défini antérieurement; en sélectionnant aussi R^1 parmi le groupe composé par SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 ou n'importe quelle autre combinaison d'eux-mêmes; en unissant éventuellement deux R^1 adjacents pour former un anneau de cyclopentadiénol polyclinique saturé ou insaturé sélectionné parmi le groupe composé par indényle, tétrahydroindényle et octahydrofluorényle, éventuellement remplacé par des groupes R^1 ;

R^{11} est hydrogène, alcoyle, cycloalcoyle, aryle, alkényle, arylalcoyle, arylalkényle ou alkylaryle de 1 à 20 atomes de carbone, linéaire ou ramifié, dont les hydrogènes sont éventuellement remplacés par des groupes SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 ou n'importe quelle combinaison d'eux-mêmes, où R est comme il a été défini antérieurement; formant éventuellement un anneau condensé au travers d'une autre liaison avec E;

E-E est $\text{CR}^{\text{IV}}_2\text{-SiR}^{\text{III}}_2$ ou $\text{SiR}^{\text{III}}_2\text{-CR}^{\text{IV}}_2$; chaque R^{III} , pouvant être égaux ou différents, est hydrogène, alcoyle, cycloalcoyle, aryle, alkényle, arylalcoyle, arylalkényle ou alkylaryle avec de 1 à 20 atomes de carbone, linéaire ou ramifié, les hydrogènes étant éventuellement remplacés par des groupes SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 ou n'importe quelle combinaison d'eux-mêmes, où R est comme il a été défini antérieurement;

R^{IV} a la même signification que R^{III} ou est un halogène; et de plus, deux groupes sélectionnés entre R^{IV} et R^{III} appartenant à E différents forment éventuellement une structure cyclique.

2. Composant de catalyseur selon la revendication 1, dans lequel la formule générale (I) M est sélectionnée parmi le groupe composé de zirconium, titane ou hafnium.

3. Composant de catalyseur selon la revendication 1, dans lequel le groupe d'union E-E est $\text{CR}^{\text{IV}}_2\text{-SiR}^{\text{III}}_2$.

4. Composant de catalyseur selon les revendications 1-3, dans lequel R^{II} est terc-butyle.

5. Système catalyseur comprenant un cocatalyseur sélectionné parmi le groupe composé de: alcoylealuminoxane, aluminoxane modifié et composé de bore, et un composant de catalyseur selon les revendications 1-4.

6. Système catalyseur selon la revendication 5, dans lequel le cocatalyseur est sélectionné parmi le groupe composée de: méthylaluminoxane, éthylaluminoxane, tétraquis (phénylpentafluorure) borate N,N-diméthylanilinium et tris-pentafluorurphénylborane.

7. Processus pour obtenir des polioléfines en solution, en suspension, en phase gazeuse à basses et hautes pressions et températures ou en masse à haute pression et à haute et basse température, dans lequel la température varie entre -60°C et 300°C , la pression varie entre 1 et 4000 atmosphères, comprenant l'utilisation du système catalyseur selon les revendications 5-6.

8. Processus pour obtenir des polioléfines selon la revendication 7, dans lequel la température de polymérisation varie entre -60°C et 300°C , la pression varie entre 1 et 4000 atmosphères, la concentration de métal de transition varie entre 10^{-7} et 10^{-3} M, le cocatalyseur est un complexe organique d'aluminium et la relation molaire de cocatalyseur/métal de transition varie entre 10 et 10000.

9. Processus pour obtenir des polioléfines selon la revendication 8, dans lequel la température varie entre -40°C et 220°C , la concentration de métal de transition varie entre 10^{-6} et 10^{-4} M, le cocatalyseur est un complexe organique d'aluminium et la relation molaire de cocatalyseur/métal de transition varie entre 500 et 1500.

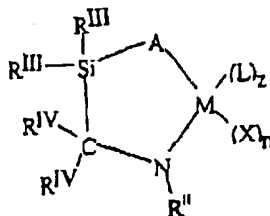
10. Processus pour obtenir des polioléfines selon la revendication 7, dans lequel la concentration molaire de métal de transition varie entre 10^{-7} et 10^{-3} , le cocatalyseur est un composé de bore et la relation molaire de cocatalyseur/métal de transition varie entre 0,5 et 10.

11. Processus pour obtenir des polioléfines selon la revendication 10, dans lequel la température de polymérisation varie entre -40°C et 220°C , la concentration de métal de transition varie entre 10^{-6} et 10^{-4} M, le cocatalyseur est un composé de bore et la relation molaire de cocatalyseur/métal de transition varie entre 0,9 et 5.

12. Processus pour obtenir des polioléfines selon les revendications 8-11, dans lequel le monomère est éthylène.

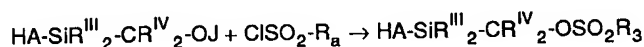
13. Processus pour obtenir des copolymères d'éthylène selon les revendications 8-12, dans lequel le comonomère est sélectionné parmi le groupe composé de : propène, 1-butène, 1-hexène, 1-octène, 1-hexadécène, 4-méthylpentène, hexadiène et styrène, ou mélanges de ceux-ci.

14. Processus pour obtenir un composé de formule :

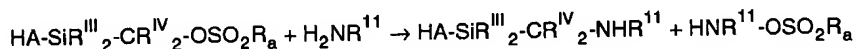


dans laquelle A, E, M, L, X, n, z, RII, RIII et RIV sont comme ils ont été définis dans les revendications 1-5, caractérisé par les étapes suivantes :

la réaction d'un composé de formule $\text{HA-SiR}^{\text{III}}_2\text{-CR}^{\text{IV}}_2\text{-CR}^{\text{IV}}_2\text{-OJ}$, où J est lithium ou hydrogène, avec alkylalcoyle sulfoné selon le schéma :

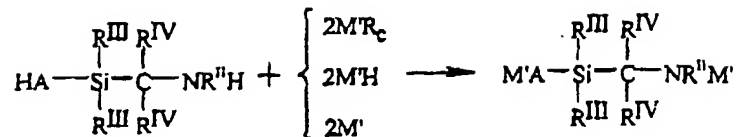


la mise en contact du produit récupéré de l'étape a) avec un excès d'une amine de formule $\text{NR}^{\text{II}}\text{H}_2$



dans laquelle R_a est un radical alcoyle $\text{C}_1\text{-C}_{20}$, perfluoralcoyle ou aryle $\text{C}_6\text{-C}_{20}$;

le traitement du composé de formule $\text{HA-SiR}^{\text{III}}_2\text{-CR}^{\text{IV}}_2\text{-NHR}^{\text{II}}$ avec deux équivalents d'un sel de métal alcalin d'alcoyle ou aryle, ou avec un hydruide de métal alcalin ou un métal alcalin selon le schéma suivant :



dans lequel R_c est alcoyle $\text{C}_1\text{-C}_{20}$ ou aryle $\text{C}_6\text{-C}_{20}$ et M' est sélectionné parmi le groupe composé de: Li, Na et K ; et

la mise en contact du composé de formule $\text{M}'\text{A-SiR}^{\text{III}}_2\text{-CR}^{\text{IV}}_2\text{-NR}^{\text{II}}\text{M}'$ avec un composé métallique M de formule MX_4 , ou avec un aducte de formule $\text{MX}_4\text{2L}$ ou $\text{MX}_3\text{3L}$ dans laquelle L est un éther linéaire ou cyclique.

Figure 1

